HEAVY METALS FROM POLLUTED ATMOSPHERES: BLACK CRUSTS ON LIMESTONES AS MARKERS OF ENVIRONMENTAL CONDITIONS INFLUENCE ON HUMAN HEALTH

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INTRODUCTION

Air pollution usually derives in the development of black crusts on the surface of cultural heritage materials. A methodological approach for the morphological, mineralogical and chemical characterization of black crusts developed on limestone on historic buildings of Cairo, Milano, Budapest and Madrid, besides suspended and settling particulate matter, has been carried out. By means of traditional techniques, such as POM, XRD, SEM-EDS and FT-IR, combined with innovative application of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), a complete characterization in terms of trace elements distribution (including heavy metals) from the black crusts and host limestone has been achieved. Some studied areas display high levels of pollutants and important concentration of heavy metals (Cd, Cu, Pb, Ni, Zn) in the suspended dust (El-Bady, 2014). Within laminar and dendritic black crusts high concentration of gypsum was recorded with increased amount of different elements and metals (Si, Al, Ti, Fe) especially derived from atmospheric inputs and, in particular, by anthropogenic pollution; in dust samples siliceous fly-ash particles are more common than carbonaceous ones and mineral fragments representing windblown particles were also detected (Perez-Monserrat et al., 2011; Török et al., 2011). Heavy metals content (Pb, Zn) are higher in black crust than in substrate, suggesting that polluted atmosphere has a great influence on their formation. Moreover, some specific heavy metals tend to migrate from the crust to the unaltered stone, becoming catalysts for new crust (Barca et al., 2014; La Russa et al., 2014). Black crusts composition entails markers to evaluate the major combustion sources responsible for stone decay and the changes on the used fuels over time. As trace element concentration is directly related with environmental conditions, the study of black crusts can be a marker for human health.

SAMPLING

In this work, the following samples were collected from the monuments: **a)** 4 black crust samples **[A]** taken at different heights in Milan; **b)** 12 black crust sample **[RAI-RAIT-MU]** with different morphology (black crusts and gray-brown crusts) taken at different heights in Madrid; **c)** 6 black crust sample **[TT]** taken at different heights in Budapest **d)** 2 crust samples **[AZ-MK]** in Cairo.

SEM

The oldest black crusts, which represent longer time of exposure and deposition of pollutants (Budapest and Cairo) show a dendritic and heterogeneous morphology, at times stratified, and the presence of numerous particles resulting from combustion processes, with different size (from 5 to 150 µm), shape (from spherical to sub-spherical to irregular) and surface morphology (smooth or porous).

The most recent crusts (Madrid and Milan) appear morphologically more homogeneous, with reduced thickness and abundance of smaller particles.

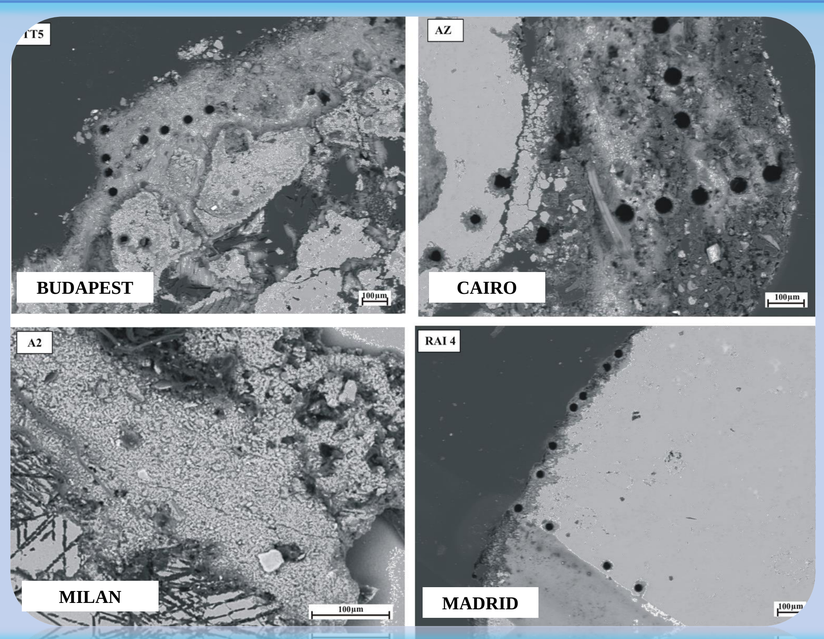

Fig. 2 BSE-SEM images of examined samples.

POM

OM and SEM-EDS provided information on the mineralogical and textural features of both substrate and black crusts. Moreover, these analysis highlighted the deterioration degree of the stone surfaces of the four monuments.

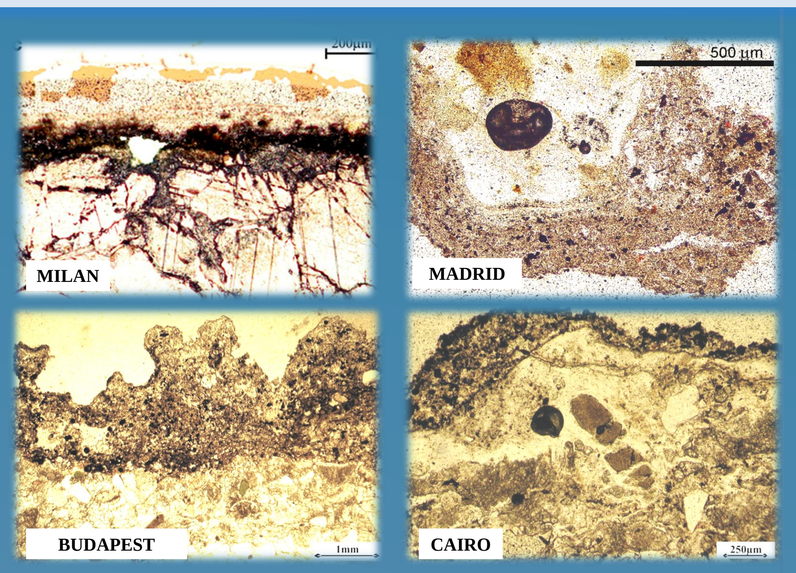

Fig. 1 Photomicrographs representative of the investigated substrates and black crusts.

The stone substrates appear to be highly degraded, with numerous microfractures, where small gypsum crystals can be identified.

The crusts composed of microcrystalline gypsum with an acicular or lamellar habitus, occur with different morphology and thicknes (from µm to cm).

FT-IR

The mineralogical composition of analyzed damage layers shows the characteristic absorption peaks of **gypsum**. In some samples calcium carbonate, quartz and oxalate are also present (Table 1). Peaks of calcite and quartz can be certainly ascribable to the underlying substrate, while the presence of oxalate can be due to restoration works carried out in the past, or the activity of microorganism colonies, or deposition of pollutants.

Table 1 The mineralogical composition of analyzed damage layers.

Monument	Gypsum (1109, 667 and 596 cm^{-1})	Calcium carbonate (1409, 871 and 710 cm^{-1})	Oxalate (1630, 1320 and 780 cm^{-1})
Milan	X	X	X
Budapest	X	X	X
Cairo	X	X	
Madrid	X	X	X

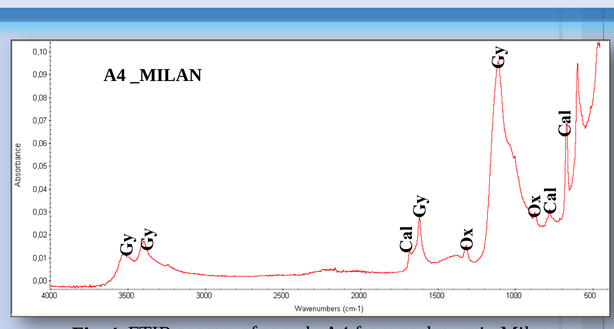

Fig. 4 FTIR spectra of sample A4 from sculpture in Milan

LA-ICP/MS

The binary diagrams (As *vs.* Pb, Cu *vs.* Zn and Ni *vs.* V) of Fig. 4 show the compositional differences between crusts, altered substrate and unaltered substrate.

On the whole, data obtained suggest that concentrations of heavy metals in the crusts and the altered substrate are higher than those in substrates.

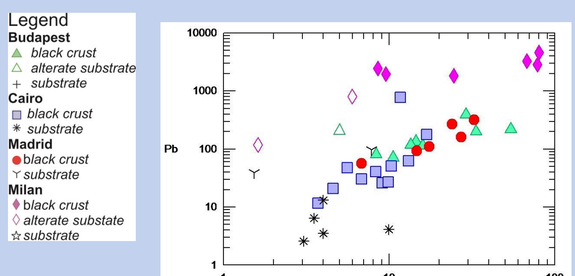

Fig. 4 As *vs.* Pb (a), Cu *vs.* Zn (b) and Ni *vs.* V binary diagrams for black crusts , altered substrate and unaltered substrate of all samples analyzed by LA-ICP-MS.

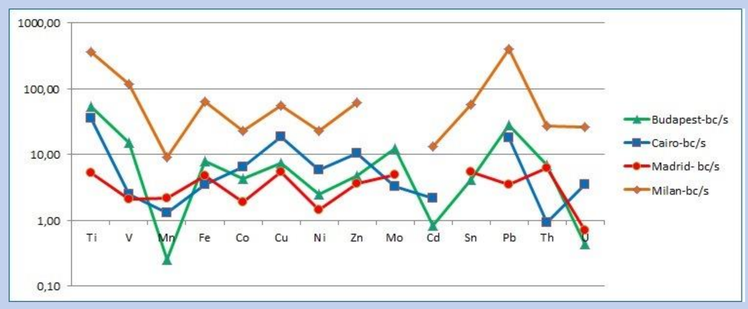

Fig. 5 Spider diagrams (logarithmic scale) of mean values of trace element concentrations in black crusts normalized to the unaltered substrate for samples.

CONCLUSIONS

The complete characterization of the damage layers provided information on their chemical composition, the state of conservation of the underlying substrates and the interactions between crusts and stones.

In particular, the geochemical study in terms of trace elements revealed that all crusts are enriched in heavy metals (As, Cd, Cr, Cu, Ni, Pb, Sb, Sn, V and Zn) compared to substrates.

The different concentrations of such elements in all analyzed crust samples can be ascribed to several factors, such as: height of sampling, morphology of the sampled surfaces (vertical or horizontal), exposure to atmospheric agents as well as to direct (road traffic) or indirect (industries) sources of pollution, accumulation time of pollutants on the surface, wash out and particulate air pollution. Specifically, the crusts collected at lower heights resulted to be mainly influenced by mobile sources of pollution (vehicular), while samples taken at higher heights are generally mostly affected by stationary combustion sources. In some cases, the detailed analysis of multilayered crusts contributed to recognize the variation of combustion sources responsible for the deterioration of surfaces over time. In addition, the possibility of analyzing altered portions of the substrate permitted to observe that some elements (Zn, Cu and Ni) show concentrations similar and, sometimes, higher than the overlying crusts. This result can be explained by the geochemical mobility of such elements (at specific environmental conditions), which accelerate the process of sulfating, rapidly promoting the formation of new layers of crust.

In conclusion, the study of black crusts and altered substrates in terms of trace elements may provide information useful to understand the influence of the pollutants in the genesis of such degradation forms.